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16. ABSTRACT

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JOURNAL ARTICLE

MASS BALANCE MODELING OF HEAVY METALS IN SAGINAW BAY, LAKE HURON

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ABSTRACT. *During the period 1976-1978, a study of hazardous materials in Saginaw Bay was conducted. This study included the fate and distribution of cadmium, copper, lead, and zinc in the bay. A spatially segmented, dynamic mass balance model was developed to describe concentrations of metals and suspended solids in the water column and in the sediments. A wind-driven resuspension mechanism was used to describe the sediment-water interactions. The distribution of metals in the water column was determined by equilibrium partitioning between the ambient suspended solids and the dissolved phase. Model output was calibrated to field data for the principal variables. Independent validation was obtained by comparing partition coefficients from the calibration to those calculated directly from the field observations. It was found that suspended solids were important in controlling the water column concentrations of the metals. The degree of control was a function of the partition coefficient between the metal and the solids, and the concentration of the solids. Adsorption of the metals to the solids was found to result in decreases to metals concentrations due to net sedimentation, as well as increases due to wind-driven resuspension. On an annual average basis, the net flux of the particulate components of all four metals was from the water column to the sediments except for copper in 1977.*

ADDITIONAL INDEX WORDS: Sediment, resuspension, partitioning, adsorption, flux.

INTRODUCTION

Saginaw Bay is a shallow extention of Lake Huron. The Saginaw River basin (Fig. 1) is the major source of pollutant loading to Lake Huron. The effects of this input on the Saginaw Bay-Lake Huron system have been studied for the case of eutrophication (Smith *et al.* 1977, Bierman *et al.* 1980). However, studies on toxic substances in the bay were extremely limited until 1976. The sparse data that were available (Bratzel *et al.* 1977) indicated that cadmium, copper, lead, and zinc were present in the bay in measurable quantities. Industrial applications involving these metals are known to occur in the basin and include electroplating, die casting, and the manufacture of paints and electrical products. Biologically, cadmium and lead are non-essential and non-beneficial (Lehninger 1970). Zinc and copper are essential trace elements but can be toxic in high concentrations (Horne and Goldman 1974).

In 1976, a sampling and analysis project was undertaken to determine the levels, sources, and distribution patterns of cadmium, copper, lead, and zinc in Saginaw Bay, Lake Huron. The results of this project were synthesized within a dynamic mass balance modeling framework. The ultimate objective of this study was to relate mass inputs of trace metals to observed water column concentrations by tracking the fate and transport of the metals as a function of space and time.

Valuable insights can be gained about the distribution and fate of these metals by using a mass balance approach. Modeling results can help to identify the relative importance of the major processes which determine the observed concentra-

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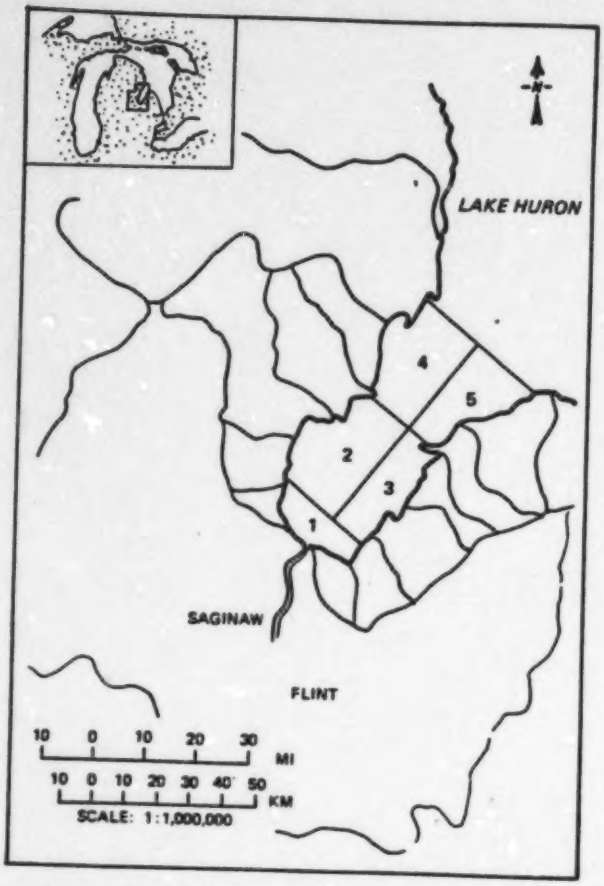

FIG. 1. The Saginaw basin (model segments are numbered 1–5).

tion distributions in space, as well as time. This information can be useful in the development of management strategies for controlling heavy metals, or for identification of future research needs. The successful application of a mass balance model to a physical system depends greatly on the available data. An important emphasis of this paper is the statistical treatment of these data to maximize the useful information.

This paper will first describe the model development and data base generation necessary for this study. The application of the dynamic mass balance to the system will be discussed, including the process of calibration. Finally, a discussion of the results wil be presented and a comparison will be made to other studies.

MODEL DEVELOPMENT

Conceptual Approach

A three-stage approach was used in the development of the metals mass balance model. In the first stage, the water transport effects in terms of advection and dispersion were quantified independently using conservative tracers. Since metal distribution is also influenced by adsorption and desorption on both inorganic (Holmes *et al.* 1974, Rohatgi and Chen 1975) and organic (Conway and Williams 1979) particles, the second stage involved a dynamic mass balance for suspended solids in the water column and sediment. The solids model was driven by output from the conservative tracer model. The final stage was the coupling of a metals mass balance to the suspended solids mass balance through an equilibrium partition coefficient between dissolved and adsorbed metal. The overall model described the fate and transport of the metal with a minimum of assumptions in terms of the available field data. A schematic diagram of this coupled model is shown in Figure 2. The details of the various interactions are described below.

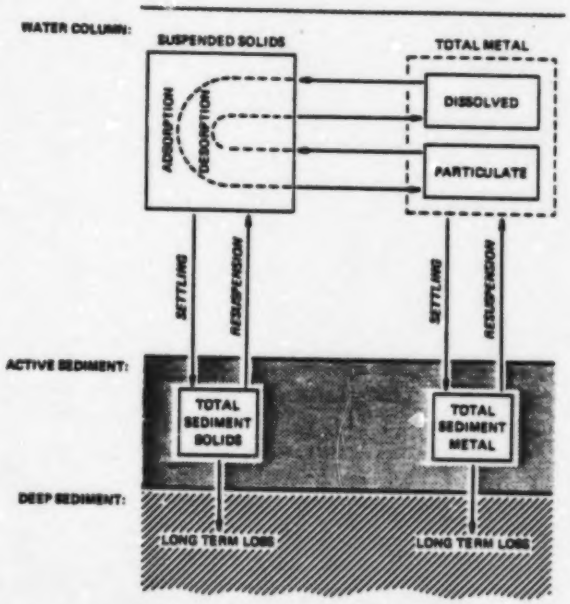

FIG. 2. Schematic diagram of metals mass balance model.

Space and Time Scales

Saginaw Bay is approximately 82 km long and 42 km wide. The horizontal gradients in water quality parameters in Saginaw Bay are large, ranging from degraded water quality in the inner bay due to input from the Saginaw River, to high quality water in the outer bay due to Lake Huron (Smith *et al.* 1977). In ther vertical direction, the bay is generally well-mixed. For these reasons, the bay was divided into five spatial segments (Fig. 1), each containing water masses that were assumed homogeneous (Bierman and Dolan 1980). The average depth of inner Saginaw Bay (Segments 1-3) is 6 m, while that of outer Saginaw Bay (Segments 4-5) is 15 m. This segmentation scheme was based partly on observed differences in water quality, and partly on a decision to minimize computational complexity. The components of the mass balance detailed in this section were used to describe the dynamics of solids and metals concentrations in the water column of each of these segments and in the sediment beneath each segment. The calculations were made on a daily basis and model output was compared to data in time periods for which it was available (every 3 weeks during the field season).

Process Mechanisms

Advection and Dispersion: The basic equation for determination of advective and dispersive transport effects with conservative tracers was:

$$V\frac{dc}{dt} = \sum_{i=1}^{n} f(Q_i, E_i, C_i) + W \qquad (1)$$

The function, f, which represents the net effect of advection and dispersion in the water column was the same as that used by Richardson (1976). The tracer used for 1976 was chloride ion, while for 1977 and 1978 conductivity was used. Concentrations of the tracers were available at the same frequency and location as the suspended solids and metals.

A version of the mass balance model based on Equation (1) was calibrated by adjusting flow rates and dispersions among model segments until calculated concentrations of tracer agreed with actual observations. The resultant flows and dispersions were then used to drive the suspended solids and metals mass balances.

Mass balance for suspended solids: The model used for the suspended solids and metals mass balance was based on the conceptual approach of Lorenzen *et al.* (1976) for total phosphorus. The following modifications were made in the present application:

1. Loading rates were considered time-variable.
2. Particulate sedimentation was considered to depend on a power function, not a first-order function.
3. The resuspension term was considered to be a function of wind speed.

The mass balance equation for each water column segment had the following form:

LIST OF SYMBOLS

A	Surface area of the precipitation collector in km².
C	Suspended solids concentration in the water column in kg/L.
C_D	Concentration of dissolved metal in the water column in μg/L.
C_s	Concentration of solids in the sediment in kg/L.
C_T	Concentration of total metal in the water column in μg/L.
C_{Tc}	Concentration of total metal in the precipitation sample collector in μg/L.
C_{Ts}	Concentration of total metal in the sediment in μg/L.
$\frac{dC_{(\ )}}{dt}$	The derivative of concentration with respect to time.
D	Depth of water in a segment in meters.
D_s	Depth of sediment in a segment in meters.
E_i	Dispersion at the ith interface of a segment in m³/sec.
F	Atmospheric flux of metal to the bay in μg/day/km².
k_B	Sediment burial rate in m/sec.
k_p	Partition coefficient in L/kg.
k_R	Sediment resuspension velocity in m/sec.
k_s	Normalized settling velocity in m/sec.
N	Empirical constant (unitless)
Q_i	Advective flow across the ith interface of a segment in m³/sec.
v_s	Variable settling velocity.
V	Volume of water in a segment in m³.
V_c	Volume of atmospheric sample collected in liters.
V_s	Volume of sediment in a segment in m³.
W	Loading of suspended solids in MT/day.
W_T	Loading of total metal in mg/day.
$\sum_{i=1}^{n} f(Q_i, E_i, C_i)$	Function of advective flow, dispersion and neighboring segment concentrations that describes mixing effects on segment concentrations.
n	Total number of neighboring segments.

$$V\frac{dC}{dt} = \sum_{i=1}^{n} f(Q_i, E_i, C_i) + W - \frac{V\,C\,v_s}{D} + \frac{V_s\,C_s\,k_R}{D_s} \quad (2)$$

The solids concentration in the sediment was calculated by a mass balance on each sediment compartment:

$$V_s\frac{d\,C_s}{dt} = \frac{V\,C\,v_s}{D} - \frac{V_s}{D_s}C_s\,(k_R + k_B) \quad (3)$$

Equations (2) and (3) were coupled through the two variables for suspended solids concentrations, C and C_s.

Variable settling velocity: Richardson *et al.* (1980) used a version of the mass balance for suspended solids which included a variable settling velocity dependent upon the concentration of suspended matter in the water column. This was done to implicitly account for differences in settling velocities among the different size fractions of suspended solids in the water column. It was reasoned that the larger particles that are in suspension when solids concentrations are high would settle faster, and the opposite would be true for finer particles. The following parameterization was used to determine the settling velocity at any time:

$$v_s = k_s \cdot C^N \quad (4)$$

Time variable resuspension: Previous experience with a dynamic mass balance for total phosphorus in Saginaw Bay (Dolan *et al.* 1980) had shown that there was a significant source of total phosphorus from resuspended sediment. These particulates were shown to be correlated with wind events (Chartrand 1978). As the sediments in Saginaw Bay were known to contain reservoirs of each of the metals studied, it was decided to include a time-variable resuspension mechanism as a function of wind speed. A threshold mechanism was used because it was consistent with observational experience over the course of many sampling cruises on Saginaw Bay since 1974. If the average daily wind speed was below a specified threshold value, the apparent net resuspension velocity of the sediments was taken to be zero, i.e., no resuspension occurred. If the wind speed exceeded this threshold value, the apparent resuspension velocity was taken to be non-zero. The value of the apparent net resuspension velocity was determined by calibration.

Sediment burial: As shown in Figure 2, the sediment was divided into two layers: the "active" sediment layer and the "deep" sediment layer. The "active" layer was operationally defined as the surficial sediment layer subject to potential resuspension. The depth of this layer was taken to be 10 cm based on work by Robbins (1980) on the depth of benthic activity. Solids were transported from the active layer to the deep layer by the process of long-term burial. This loss from the active layer was parameterized as an apparent settling of solids out of the active layer in a fashion similar to that used by DiToro and Connolly (1980) for Lake Erie.

Equilibrium partitioning of metal on solids: The interaction of metal with suspended solids was described by equilibrium partitioning between adsorbed and desorbed phases. O'Connor and Connolly (1980) discussed the conditions under which this assumption is valid. Richardson *et al.* (1980) used this assumption for partitioning PCB in Saginaw Bay. For situations where this assumption is valid, the concentration of dissolved metal is given by (Wolfe *et al.* 1977):

$$C_D = \frac{C_T}{(k_p\,C + 1)} \quad (5)$$

This equation is identical to a linear adsorption isotherm if there is negligible competition between different trace metals for available surface sites for adsorption (Oakley *et al.* 1981). As the suspended solids concentration in the bay is approximately four orders of magnitude higher than any of the metals, the assumption of negligible competition is a good one and the partition coefficient, k_p may be thought of as the equilibrium constant for adsorption.

Metals mass balance: Mass balance equations similar to Equations (2) and (3) were defined for both the total metal in the water column, and in the sediment:

$$V\frac{d\,C_T}{dt} = \sum_{i=1}^{n} f(Q_i, E_i, C_{T_i}) + W_T - \frac{V(C_T - C_D)\,v_s}{D} + \frac{V_s}{D_s}k_R\,C_{TS} \quad (6)$$

$$V_s\frac{d\,C_{TS}}{dt} = \frac{V\,(C_T - C_D)\,v_s}{D} - \frac{V_s}{D_s}C_{TS}\,(k_R + k_B) \quad (7)$$

The mass balance for dissolved metal follows from differentiation of Equation 5:

$$V\frac{dC_D}{dt} = V\frac{dC_T}{dt}\frac{1}{(k_p C + 1)} - V\frac{dC}{dt}\left(\frac{k_p C_T}{(k_p C + 1)^2}\right) \quad (8)$$

As is shown in Figure 2, particulate metal was assumed to track with suspended solids in the water column. Also, it was assumed that all metal in the sediment was associated with solids. No explicit consideration was made of dissolved metals in the sediments. Thus, the same settling velocities, resuspension velocities, and sediment burial rates were used for metal as for suspended solids.

The five differential equations (Equation 2, 3, 6, 7, and 8) constituted the overall dynamic mass balance model used. These equations were solved using finite difference methods and a 4th order Runga-Kutta integration routine. Solutions for different years were coupled for each metal; i.e., the final condition for a given year was used as the initial conditions for the subsequent year.

METALS DATA BASE

During the period 1976-1978, approximately 20,000 data points were acquired on a 30-station sampling grid (Smith *et al.* 1977) during a total of 37 separate cruises. The data were used to either specify model forcing functions or to compare with model output in the calibration mode. Forcing functions included loading rates from tributaries and the atmosphere, boundary conditions at Lake Huron, advective flows and bulk dispersions among the different spatial segments, daily average wind speed values, and ice cover information.

The observed data on total and dissolved metals used in the calibration were taken primarily from the study by Rygwelski *et al.* (1980). Some additional information was available on the observed concentration of total metal in the sediment. The concentration of total zinc, lead, and copper in the sediment was obtained from work by Robbins (1981). Figure 3 is a concentration contour map for zinc in 1976. Similar maps were available for copper and lead. Concentrations for metals beneath Segment 2 were 100, 50, and 37.5 μg/gram for zinc, lead, and copper, respectively.

No contour maps were available to estimate sediment concentrations of cadmium. Therefore, levels were initially estimated by comparison to the data by Coggins *et al.* (1979). In this study, zinc, lead, and copper levels were reported that were

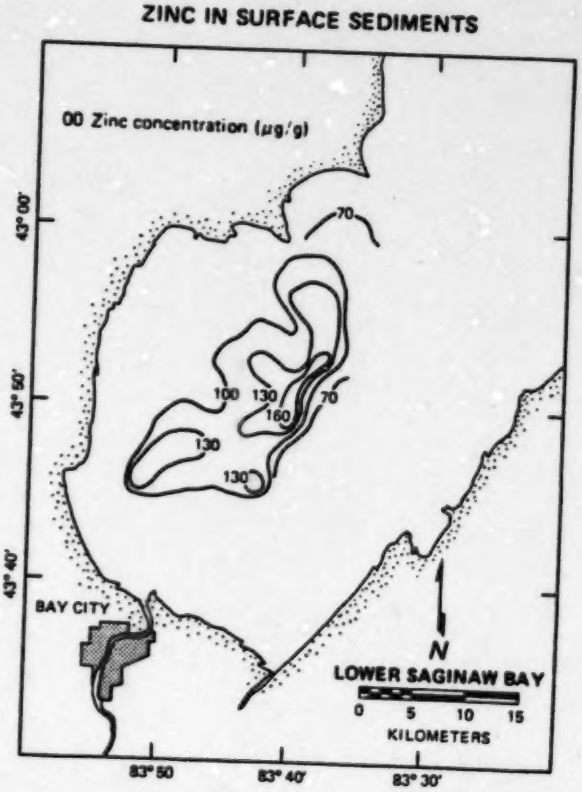

FIG. 3. Surficial sediment concentration contours for zinc, Saginaw Bay, 1976.

similar to those observed in Saginaw Bay sediment. The cadmium concentration reported was thus used as an initial estimate of the concentration of cadmium in the Saginaw Bay sediments. The ratio of the estimates used for cadmium to the other metal concentrations in the sediment was roughly similar to the ratio of cadmium to the other metals observed in the water column.

The Saginaw River was sampled intensively during the study period to determine daily metals concentrations. For each year that a metal was studied, at least 150 measurements on different days were performed.

Bulk precipitation samples were collected on a monthly basis at several sites around Saginaw Bay. The concentration of metals in these samples, as well as the volume of rain water collected, were used to estimate the monthly flux of each metal to each segment of the Bay for the study period.

STATISTICAL REDUCTIONS AND ANALYSES

Data Screening and Display

As both total and dissolved concentrations for each metal were to be compared to model output, problems arose when observed dissolved concentrations were higher than the observed total levels. This occurred occasionally during the study due to problems with quality control, such as reagent blanks, filter contamination, etc. However, if the true total and dissolved concentrations in the water column were close to one another, then there was always a possibility that the measured dissolved would be higher than the total solely due to random errors in sampling and analysis procedures. A screening method was designed that rejected dissolved concentrations that were significantly higher than the corresponding total concentration for a given sample, but otherwise retained both concentrations. The decision rule used was to reject the dissolved concentration if it was higher than the total value with 95% confidence. This screening was possible because an estimate of the standard deviation of each measurement was available. The output of this screening procedure was then displayed graphically by cruise and segment using notched box plots (Fig. 4).

The box plots have been shown to be useful in displaying water quality data that are highly skewed (Rodgers and Kasprzyk 1981). For many of the sampling cruises and station groupings, the present metals data are highly skewed because many of the individual measurements are at or near analytical detection limits. This was especially true in the outer portion of the Saginaw Bay. Detection limits were 0.01 μg/L, 0.10 μg/L, 0.09 μg/L, and 0.02 μg/L for cadmium, copper, lead, and zinc, respectively.

Calculation of Observed Partition Coefficients

"Observed" partition coefficients were calculated from the measured concentrations of total and dissolved metal and suspended solids using a rearranged version of Equation (5):

$$k_p = \frac{\frac{C_T - C_D}{C}}{C_D} \qquad (9)$$

The accuracy in determining k_p can be very sensitive to the proportions of the particulate and dissolved phases. If C_D exceeds C_T, the partition coefficient becomes negative, which has no physical meaning. At the opposite extreme, low values of C_D will cause the partition coefficient to become unrealistically large. Consequently, a special screening procedure was developed to produce a data set from which to calculate partition coefficients.

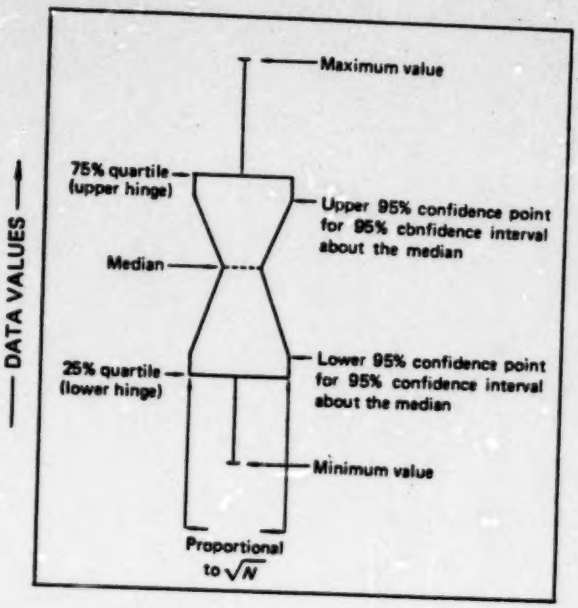

FIG. 4. The notched box plot.

High values of dissolved metal were rejected if they were not less than the corresponding total metal concentration at the 95% confidence level. Low values of dissolved metal were rejected if the blank correction was greater than one-half of the measured value. The results of the partition coefficients calculated from this screened data set for Segment 2 are shown in Table 1.

MODEL CALIBRATION

The goal of model calibration is to obtain best possible correspondence between model output and observed data for the principal variables. The procedure is to assemble all of the information on forcing functions necessary to drive the model, to define criteria by which the comparison of model output to observed data will be judged, and then to evaluate this comparison and adjust model param-

TABLE 1. Observed partition coefficients (k_p) for copper, cadmium, zinc, and lead, 1976-1978, Saginaw Bay, Segment 2.

	1976	1977	1978
Copper	-	156,000	100,000
Cadmium	224,000	-	-
Zinc	296,000	277,000	412,000
Lead	-	438,000	418,000

eters to improve it. During Stage 1 of this study, the model was calibrated to conservative tracer data by adjusting advection and dispersion values for each segment. Stage 2 involved calibration to suspended solids data by adjusting the variable settling, resuspension velocity, and sediment burial parameters. Finally, Stage 3 was actual calibration to data for each metal by adjustment of the partition coefficient.

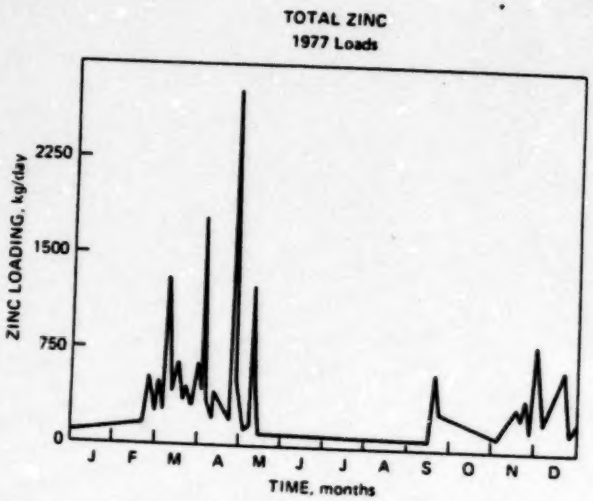

FIG. 5. 1977 tributary loading for total zinc.

Forcing Functions

All model forcing functions were specified on a time-variable basis using scales consistent with their observed variability. The most important forcing functions for the metals are the tributary and atmospheric loading rates. It should be noted that there are no known point sources of metals on Saginaw Bay itself and that the Saginaw River is the only tributary that contributes metals to the bay in any significant amounts.

The measured river concentrations were combined with daily flow rates for the Saginaw River from the U.S. Geological Survey to determine daily loading rates for each metal for each year. This method is described in Bierman *et al.* (1980). Figure 5 is a typical tributary forcing function that was determined in this manner.

The following equation was used to estimate the atmospheric flux of each metal to the Bay:

$$F = \frac{C_{Tc}\, V_c}{A} \qquad (10)$$

The flux estimate for each station was then applied to the spatial segment nearest it to calculate the monthly atmospheric loading rate for that segment. For months in which more than one flux estimate per segment was available, the average was used.

As Lake Huron proper was not included explicitly in the Saginaw Bay mass balance model, the boundary conditions at the Saginaw Bay/Lake Huron interface must be specified. This was done by using the average of the measured concentrations at stations on the outermost transect across the mouth of the bay.

Estimates of the daily average wind speed over the bay were needed to specify the days on which resuspension of bay sediment occurs. Wind speed measurements were taken at Tawas and Bay City by the National Weather Service at 2- or 3-hour intervals during the entire study period. The data from Bay City were used primarily, as they was more complete, with the Tawas data to fill in gaps when they occurred. Daily averages of the wind measurements were calculated and input to the mass balance model.

Ice cover information for Saginaw Bay was required for two reasons. As the resuspension of bottom sediment was considered to be wind-dependent, ice cover would essentially halt this phenomena. Also, the atmospheric loading rates of metals were input to the model on a monthly basis. For those months that a segment was ice covered, the atmospheric component of the metals load was assumed to build up on the ice until breakup. Then the accumulated load was input to the segment at once. Weekly records of ice cover on Saginaw Bay were available from the National Oceanic and Atmospheric Administration's Great Lakes Environmental Research Laboratory. These were used to specify to the model the days of ice formation and ice breakup for each segment in each year.

Knowledge of the depositional zones in Saginaw Bay was also important forcing information

(Robbins 1981). In the inner bay, no deposition was observed in Segments 1 and 3. This is due to the shallow nature of these segments (1–2 m in depth) as opposed to Segment 2 (4–15 m in depth) as well as the phenomenon of wind-driven resuspension which tends to scour sediment and re-deposit it in Segment 2. This is probably an example of "focusing," i.e., the hydrodynamics and morphometry of the bay tend to "focus" the sediments into Segment 2 (Thomas *et al.* 1973). This information was used to force the model with higher resuspension rates and no long term sediment burial in Segments 1 and 3.

Calibration Criteria

As the foregoing suggests, Segment 2 is important both in terms of its water quality and the sediment beneath it. Nine of the 30 sampling stations for this study were located in model Segment 2. As can be seen from Figure 3, most of the sediment metal concentration data came from Segment 2. Also, model calculations for this segment are not directly influenced by the boundary interaction with Lake Huron, for which no actual measurements of total and dissolved metal concentrations existed. For these reasons, Segment 2 was chosen as the highest priority segment in the calibration of the mass balance of each metal.

The calibration strategy was to minimize the sum of the squares of the differences between model output and observed data for suspended solids and total and dissolved metal for each sampling cruise during the study period in each segment, with Segment 2 having the highest priority. The calibration for suspended solids was accomplished by adjusting the variable settling parameters, k_s and N, the resuspension parameters, k_R and the threshold wind, and the sediment burial parameter, k_B, until the sum of squares was minimized. The calibration for metals was obtained by using the parameters from the suspended solids calibration and adjusting the partition coefficient, k_p, until the minimum sum of squares was found.

Calibration Results

The calibration results are shown as plots of model output and data. For the tracer and suspended solids, the observed data were plotted for each cruise as the mean of the data in the segment ± a standard error. The metals data were presented using box plots, as discussed earlier.

Figures 6 and 7 show the calibrations for

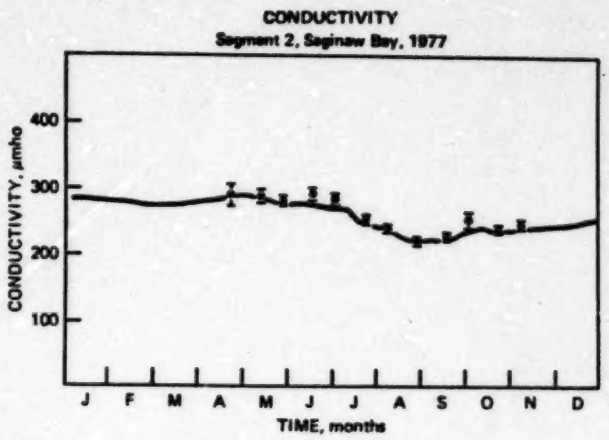

FIG. 6. 1977 conductivity calibration, Segment 2.

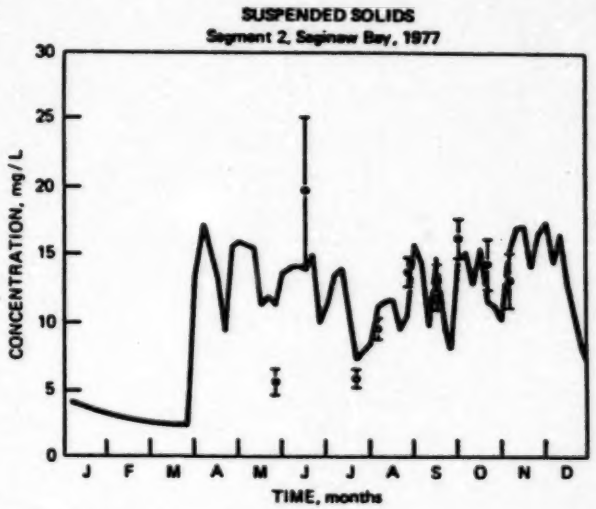

FIG. 7. 1977 suspended solids calibration, Segment 2.

conductivity (tracer) and suspended solids in 1977 for Segment 2. Table 2 contains the parameter values associated with the suspended solids calibration. Figures 8 through 11 present the comparisons of model output to observed data for dissolved and total metal for Segment 2 in each year. The model output represents a dynamic mass balance of dissolved and total metal in each year. The same partition coefficient, k_p, was used to describe the interaction of each metal and the solids during each year.

For comparative purposes, a model vs. data "scoresheet" is presented in Table 3. For each

TABLE 2. Calibration parameters from suspended solids mass balance model.

Maximum Settling Rate	1.4 m/day
Constants in Variable Settling Rate Expression ,	
N	2.0
k_s	3.5×10^{-4} m/day
Threshold Wind Velocity	11 knots
Resuspension Velocity, k_R	
Segment 1	4.2×10^{-4} m/day
Segment 2	1.35×10^{-4} m/day
Segment 3	3.21×10^{-4} m/day
Segment 4	3.2×10^{-6} m/day
Segment 5	4.16×10^{-5} m/day
Initial Solids Concentration in Sediment, C_s	1.8×10^{-5} mg/L
Burial Rate, k_B	
Segments 1,3	0.0 m/day
Segment 2	8.22×10^{-6} m/day
Segments 4,5	1.6×10^{-6} m/day
Depth of Sediment	
Segment 1	0.01 m
Segment 2-5	0.1 m

calibrated parameter, the percent of sampling cruises for which model output agreed with observed data to within plus or minus one standard error of the mean/median value is shown for each model segment, in each year. Note that the estimate for standard error for the metals data is the robust estimate, based on the box plot, while for chloride, conductivity, and suspended solids it is the conventional one:

$$S.E. = \frac{S}{\sqrt{n}}$$

where S is the sample standard deviation, and
n is the number of samples.

As a result, model agreement with data occurs when the calculated value is within the error bars for chloride, conductivity, or suspended solids, and within the "box" for total and dissolved metal. These comparison criteria are fairly stringent. The usual 95% confidence interval is the sample mean plus or minus approximately 2 standard errors. If this interval had been used, most of the scores in Table 3 would be 100%.

Zinc: The model output for total zinc for all 3 years agreed well with the observed data for the summer and fall, but only in 1977 was there an acceptable comparison for the entire year. The observed data for the three years were quite different. In 1976 and 1978, the spring was characterized by high total zinc concentrations, while in 1977, no such peaks were observed. For 1976, there were two problems: the total zinc data were not corrected for blank values, and only data from July to December were available to estimate atmospheric loading, which is important in the spring. In 1978, the spring cruises were largely exploratory in nature and fewer stations were sampled.

The model agreed well with the observed level of dissolved zinc in Segment 2. The dissolved zinc concentrations measured during these 3 years were substantially lower than the total zinc values and, in general, less variable.

Lead: For total lead, the observed data for both years showed a fall peak. This was not reproduced well by the model. The comparison for the rest of the year was reasonable, especially in the summer. Note that the lead levels are in general much lower than the zinc levels. The dissolved lead data and model output agreed well. In both years, extremely low levels of dissolved lead were observed in Segment 2 and low levels were calculated by the mass balance model.

Copper: In both 1977 and 1978, the model output for total copper agreed with the level of the measurements, but the seasonal variability of the data was not reproduced. The observed data in 1977 were, in general, somewhat higher and more variable than in 1978.

For dissolved copper, the blank and storage problems were particularly troublesome in 1977. In fact, most of the dissolved data for that year were higher than the total. However, when these analytical problems were corrected (1978) the model and the data agreed remarkably well. Also, the variability of the data was greatly reduced. The model output indicates that a large percentage of the copper in Segment 2 was in the dissolved form. The observed data for 1978 confirm this.

Cadmium: For total cadmium, except for one cruise in the spring, the model was in excellent agreement with the observed data. For dissolved cadmium, the model output was mostly below the observed data. However, much of the dissolved cadmium data were at the detection limit of 0.01 μg/L and, therefore, the model output and data do not necessarily contradict one another.

An important component of the mass balance is the sediment concentration of total metal. The

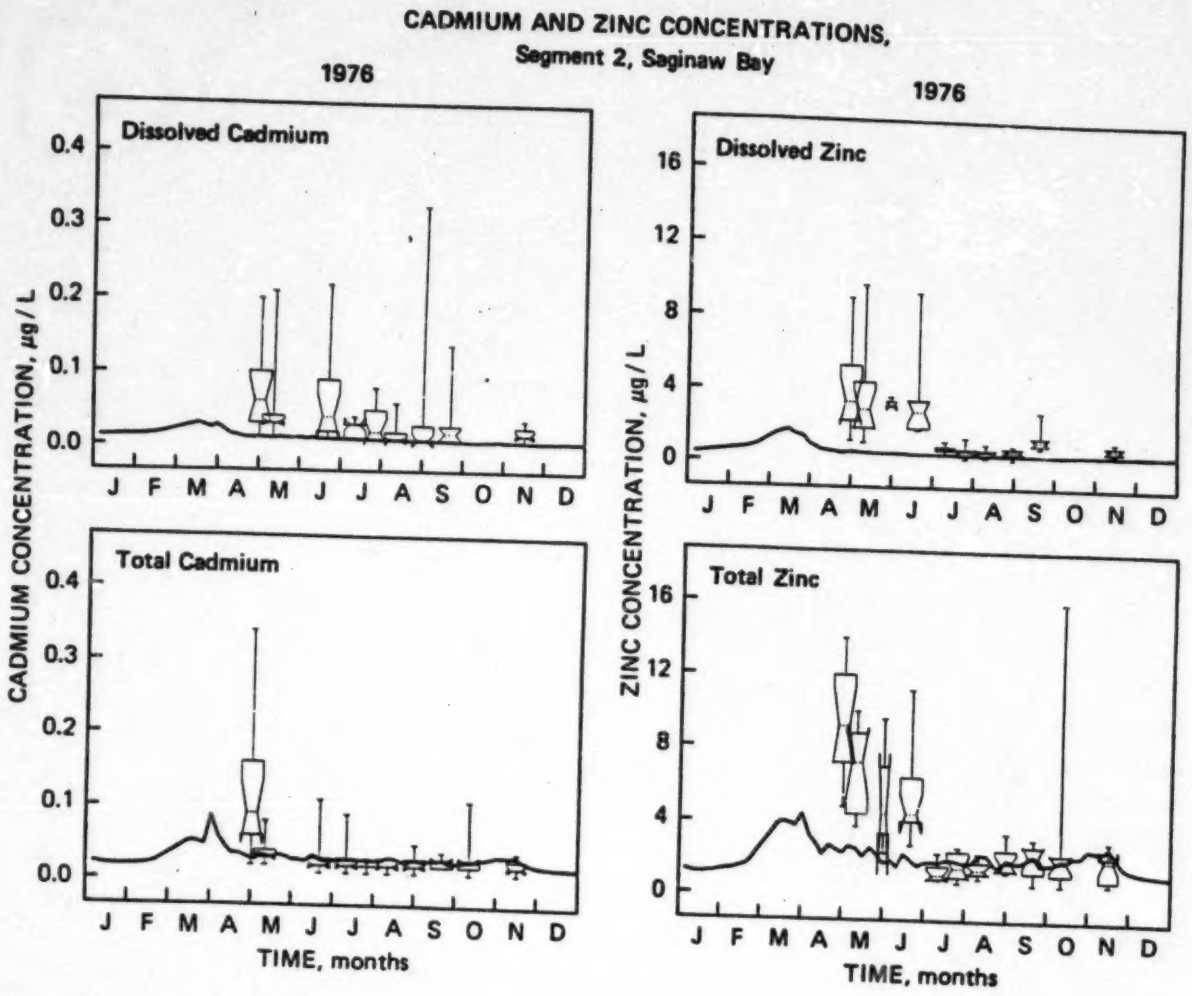

FIG. 8. 1976 cadmium and zinc concentrations, Segment 2.

observed concentrations in Figure 3 were the result of many years of metal-sediment interactions in Saginaw Bay. The model output for these sediment total metal concentrations for each metal in Segment 2 did not change appreciably from its initial value over the 2 to 3 years that were modeled. This is consistent with what would be expected given the size of the net annual flux to the sediment and the total mass of the sediment reservoir for each metal.

DISCUSSION

Internal Consistency of Results

The dynamic mass balance modeling approach used helped to synthesize a great deal of information on different chemicals in different years for a complex physical system. An important check on the internal consistency of the modeling results is the comparison between partition coefficients determined from the calibrated model, and partition coefficients determined directly from the data.

While there are differences between these two sets of k_p values, the calibration values are in the same order as the averages of the values determined from the field data for Segment 2:

	k_p, copper	<	k_p, cadmium	<	k_p, zinc	<	k_p, lead
Calculated From Field Data:	128,000	<	224,000	<	328,000	<	428,000
Model Calibration:	50,000	<	145,000	<	225,000	<	500,000

The lack of precise agreement between observed

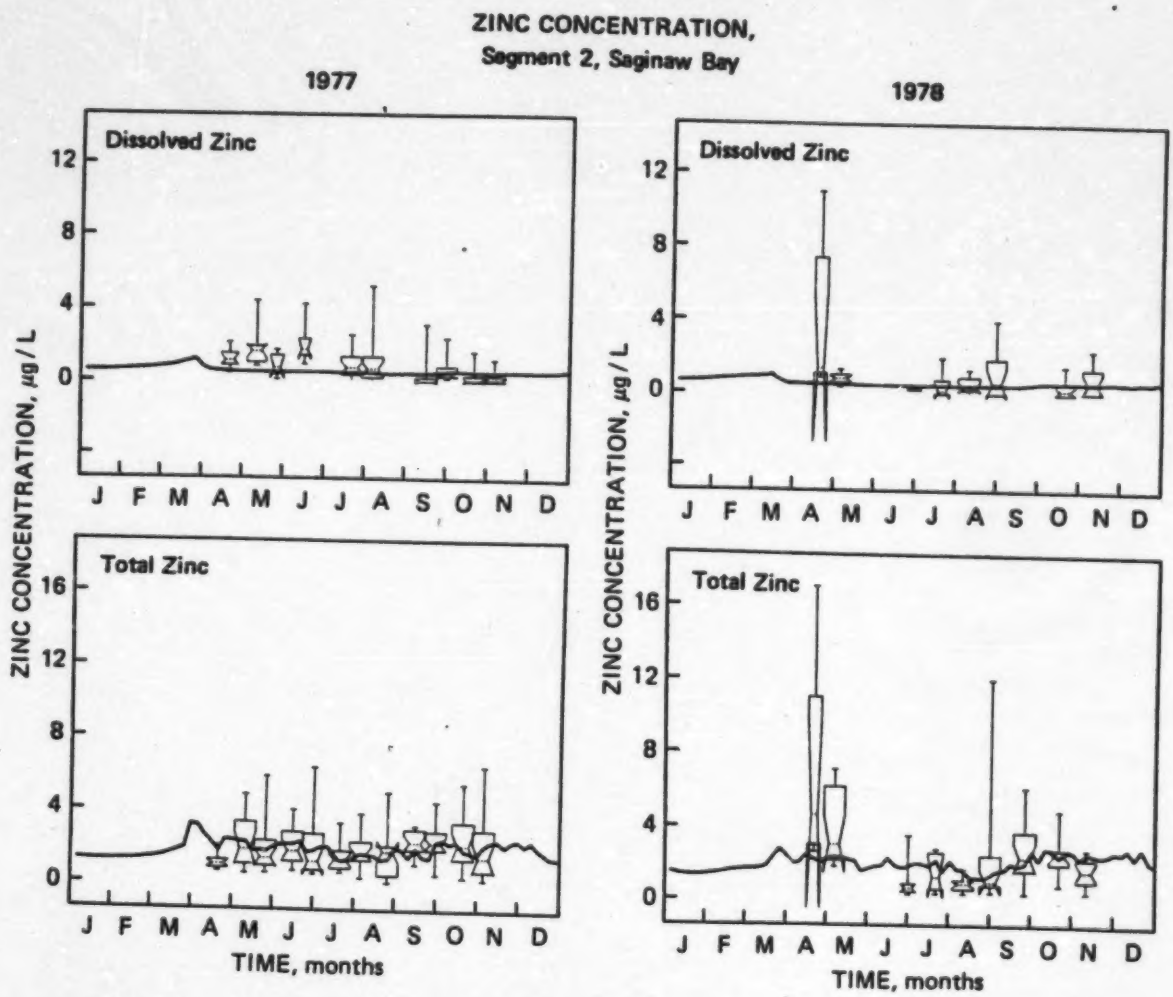

FIG. 9. 1977-1978 zinc concentrations, Segment 2.

and calibration values is in the direction that would be expected because of the bias of the screening procedure employed. For copper and zinc, the calibration values were lower than those calculated from observations. Recall that the screening procedure rejected a number of samples whose dissolved and total concentrations were not significantly different. If these samples had been included, the effect would be a decrease in the observed k_p. In the case of lead, a higher calibration k_p was found than was observed. A large number (approximately 40% of all samples) of dissolved lead concentrations were reported as less than the detection limit of 0.09 µg/L. These samples were not used in the partition coefficient calculation procedure. Had they been used, their effect would be to raise the observed k_p.

For cadmium, the problem discussed earlier of the lack of sediment concentration data dictated a different approach. An attempt was made to fix the k_p for cadmium and adjust the sediment concentrations in the model until agreement was obtained between observed water column concentrations and model output. As the calculated value of the observed annual average partition coefficient for cadmium (224,000) fell between the values for copper and zinc (128,000 and 313,000), and as the calibration k_p values for both these metals were somewhat lower than the calculated ones, a value for cadmium was interpolated assuming a down-

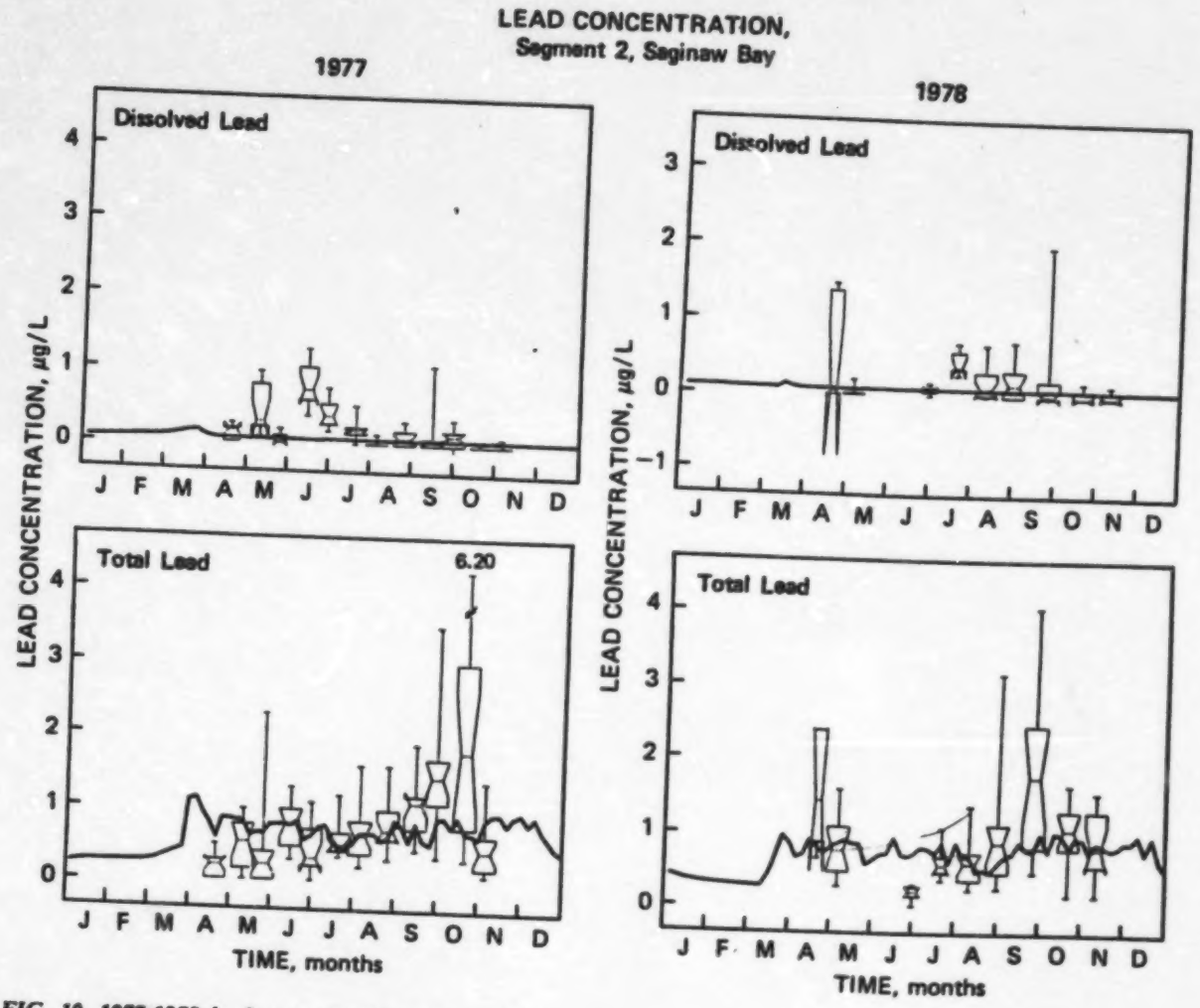

FIG. 10. 1977-1978 lead concentrations, Segment 2.

ward adjustment in the same proportion. This value, 145,000, was used in the model and the sediment cadmium concentration was adjusted until good agreement was obtained. The concentration used for the sediment beneath Segment 2 was 0.85 µg/g. This resultant assumed sediment chemistry concentration agreed with that observed by Coggins *et al.* (1979) to within a factor of 2.

Recall that, after the water transport in the model has been specified by modeling a conservative tracer and the settling and resuspension parameters have been determined in the suspended solids calibration, the only "free" calibration parameter was the partition coefficient. Thus any model uncertainties that remain after these first two calibration stages are incorporated into the calibration value for the partition coefficient. The same value for model partition coefficient was used in each year for which a particular metal was modeled.

It is useful to compare the effect of replacing the calibrated k_p value in the model with an average of the yearly observed values for each metal. When this was done, the resultant fit to observed data was reasonable. In general, the total metal scores (Table 3) were affected less than the dissolved metal scores. For zinc, the total metal scores changed by ± 10% or less, while the dissolved metal scores decreased by as much as 33% in a given segment. Scores for total copper changed by ± 28%, while

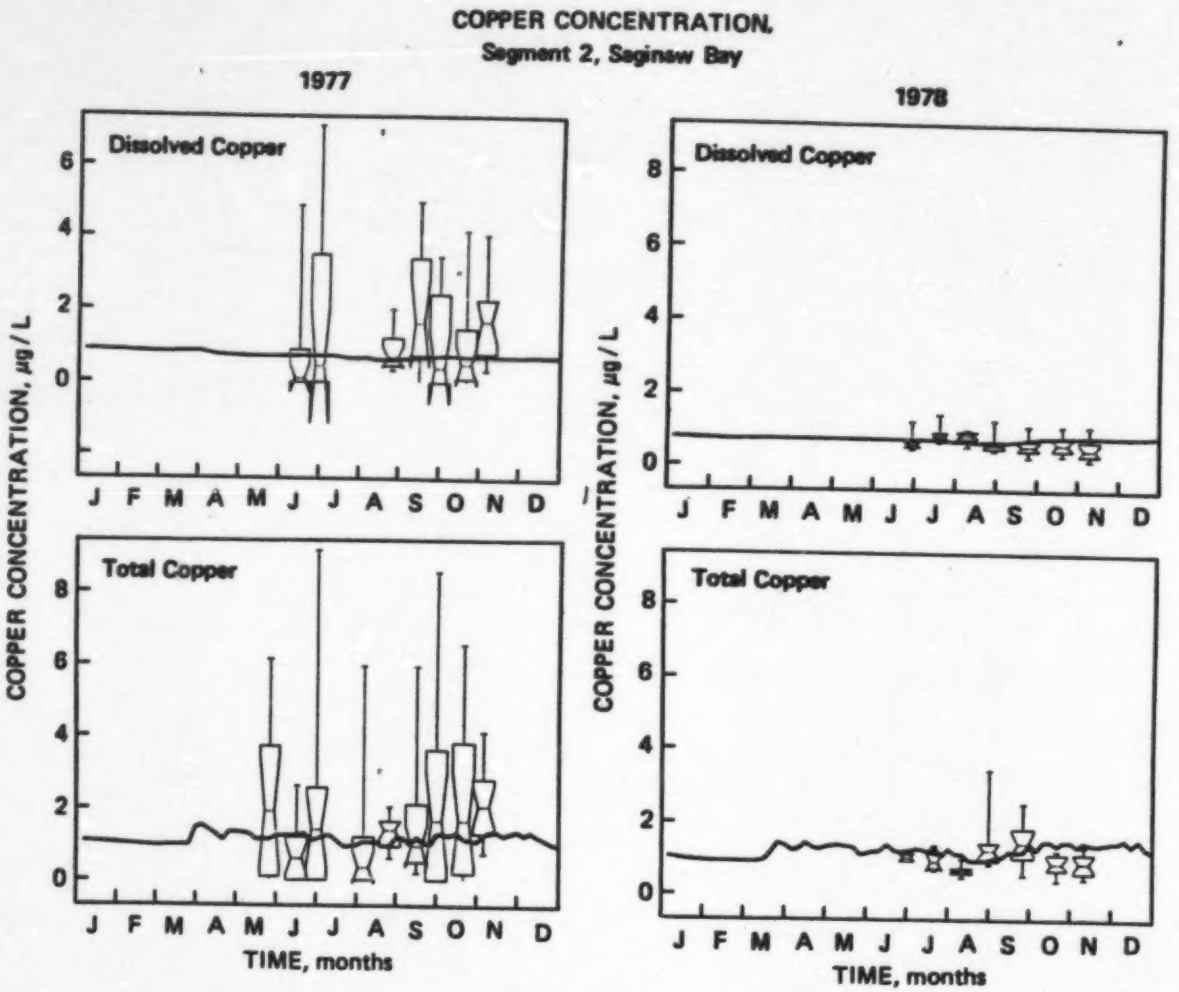

FIG. 11. 1977-1978 copper concentrations, Segment 2.

dissolved copper scores changed by ± 33%. The total lead scores dropped by as much as 28% while the dissolved lead scores decreased by as much as 33%. Although there was some improvement of scores for individual segments, the overall effect of replacing the calibrated k_p value with the average of the observed k_p values was to decrease the scores for each metal, with the dissolved metal scores dropping more.

While some of the discrepancies between observed and calibrated k_p values were due to calculation methods or analytical limitations, some of the differences were probably due to the minimum assumption approach used in developing the model. The complexity of the actual system has not been accounted for in all respects. For example, the partition coefficient is known to depend on suspended solids concentration (O'Connor and Connolly 1980). In this study, however, the partition coefficient was assumed to remain constant. Also, the sediment metals concentrations were not resolved into the particulate and dissolved phases. This would allow for the possibility of a diffusive flux of dissolved metal to the water column from the sediment.

An important simplification was the assumption that all resuspension "events" resulted in the same flux of solid material from the sediments to the water column. In fact, the degree of resuspension is more correctly a function of bottom shear stress

TABLE 3. Percent of sampling cruises for which model output was within ± one standard error of the mean/median of the data.

Parameter	Spatial Segments 1	2	3	4	5
1976					
Chloride	77	85	85	100	89
Suspended Solids	67	22	67	56	50
Total Zinc	45	55	55	67	56
Dissolved Zinc	33	30	0	13	29
Total Cadmium	33	88	70	63	100
Dissolved Cadmium	67	56	0	25	63
1977					
Conductivity	83	92	75	75	91
Suspended Solids	89	78	89	33	56
Total Zinc	67	92	92	75	82
Dissolved Zinc	56	40	56	63	60
Total Copper	73	89	100	88	67
Dissolved Copper	43	86	57	33	57
Total Lead	59	67	67	67	60
Dissolved Lead	40	59	46	86	100
1978					
Conductivity	63	75	67	100	75
Suspended Solids	83	67	83	67	40
Total Zinc	50	67	71	75	57
Dissolved Zinc	71	75	57	80	67
Total Copper	71	43	100	43	67
Dissolved Copper	71	57	80	50	60
Total Lead	75	78	71	88	43
Dissolved Lead	29	78	100	50	67

(Paul *et al.* 1982). This stress, in turn, is dependent on a number of variables including wind speed, fetch, and the condition of the sediment. Sediment conditions can vary seasonally due to benthic activity and high run-off events in the spring. The assumed constant resuspension flux could have caused some of the discrepancies between model output and data, especially during the months of April, May, and June.

The lack of a biological component for suspended solids may have introduced spatial and/or temporal uncertainties in the partition coefficient for certain metals. For example, the total lead data peaks in the fall of both 1977 and 1978 (Fig. 10). Blue-green algae, such as *Anacystis* sp., are known to absorb lead and other metals in association with phosphorus (Stoermer *et al.* 1980, Sicko-Goad and Stoermer 1979, Baxter and Jensen 1980). These algae were important in Saginaw Bay in the fall during the 3 year period. Their natural buoyancy would have resulted in lower settling rates than other particulates in the water column. Consequently, lead uptake by these algae would have had the effect of raising the effective partition coefficient during the fall periods.

One of the most interesting and potentially useful improvements in this modeling approach is the introduction of three or four particle size ranges. Each size range would have its own partition coefficient, settling rate, and resuspension rate. This is also a way of including effects of algae because a size range could be chosen to represent them.

Distribution of Metals

The use of the mass balance approach has allowed the assessment of the importance of the various sources and sinks of metals in Saginaw Bay. Table 4 presents the whole bay amounts for tributary load, atmospheric load, and loss to sediment. The loadings in Table 4 are integrals of the daily forcing functions based on data. The sediment loss amounts are output from the calibrated model. Tributary inputs represented substantial sources for all of the metals studied, but for lead and cadmium, the atmosphere was the largest source. This is in contrast to total phosphorus which has an atmospheric contribution of about 5% of the total input (Bierman *et al.* 1980).

Large percentages of cadmium (77%), lead (28-38%), and zinc (15-79%) were lost to the sediment in each year. Copper, on the other hand, exhibited little or no net loss to the sediment in the 2 years it was studied. These net losses from the water column depend on several factors, including the relative magnitude of the partition coefficient value, suspended solids levels, the degree of wind-driven resuspension, and the ratio of tributary to atmospheric input.

In 1976, the relatively high net loss of metals to the sediment corresponds to the extremely high suspended solids loading in this year (276,300 metric tonnes per year as opposed to 86,400 in 1977 and 97,300 in 1978). The greater quantity of sorbent in the water column resulted in increased sedimentation and hence, increased removal of metals from the water column. The solids loadings in 1977 and 1978 were more typical of the average annual solids loadings to the bay.

Wind-driven resuspension events substantially affected the mass flux exchanges of metals between water column and sediment. Figure 12 is a plot of model output for the daily net flux of zinc to (positive) or from (negative) the sediment in 1978. The effect of ice cover on this flux can be seen at the beginning of the year where the flux is greatly

TABLE 4. Whole system mass balances. Mass in metric tonnes (percent of total input).

Year/Metal	Total Measured Input			Total Lost to Sediment From Model Calibration Results
	Tributary	Atmosphere	Total	
1976				
Zinc	166 (83)	34 (17)	200	158 (79)
Cadmium	2 (38)	3 (62)	5	4 (77)
1977				
Zinc	86 (75)	29 (25)	115	17 (15)
Lead	17 (43)	23 (57)	40	11 (28)
Copper	15 (68)	7 (32)	22	-4 (-)
1978				
Zinc	129 (83)	28 (17)	157	61 (39)
Lead	20 (44)	25 (56)	45	17 (38)
Copper	24 (86)	4 (14)	28	0.4 (1.4)

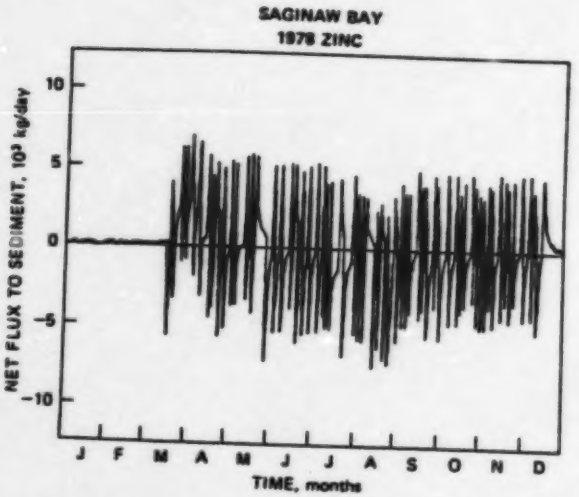

FIG. 12. 1978 daily net flux of zinc to/from sediment.

reduced. Once the ice leaves the bay in the spring, high frequency variations in net flux occur. These are caused by transient wind events which result in a net flux from the sediment, and by the concentration-dependent settling rates that quickly return most of the solids back to the sediment.

In a given year, the fractions of tributary input of metals lost to the sediment were found to be ordered as an increasing function of partition coefficient values (Figures 13 and 14). The differences between years due to different suspended solids levels and wind events may be seen by comparing Figures 13 and 14. In 1978, most of the metals loading occurred in the spring, when suspended solids levels were high. This resulted in a large metals flux to the sediment early in the year. In 1977, the loading was more uniform throughout the year, and thus the metals flux to the sediment was not as great during the same period. Although there were substantial differences between the 2 years, the ordering as a function of partition coefficient was preserved. Note that the copper fraction was often positive and that the lead fraction approached minus one. The positive fraction for copper was caused by net positive fluxes of copper to the water column on several individual days. The lead fraction approached minus one because almost as much lead was lost to the sediment as entered the bay from the tributary.

As there were major differences in the proportion of inputs from tributary and atmospheric sources among the metals (Table 4), the cumulative metal lost as presented in Figures 13 and 14 was normalized by dividing by the total tributary input. If this had not been done, less lead would have appeared to be lost on a percentage basis, and more zinc and copper would have appeared to be lost. This phenomenon is due to the substantial loading of atmospheric lead to the outer bay (Segments 4 and 5), and the fact that the principal depositional zone in Saginaw Bay underlies Segment 2. In the outer bay, the major loss mechanism is flushing by Lake Huron rather than net sedimentation. Consequently, the net metals losses to the sediment were more accurately reflected in the results contained in Figures 13 and 14.

Under certain wind and suspended solids loading conditions, it would apparently be possible to describe the whole system dynamics of a metal using the assumptions of simple dilution and

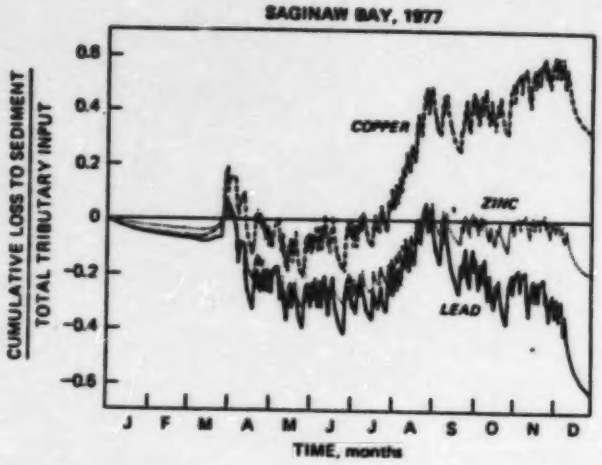

FIG. 13. Ratio of cumulative metal lost to tributary input, Saginaw Bay, 1977.

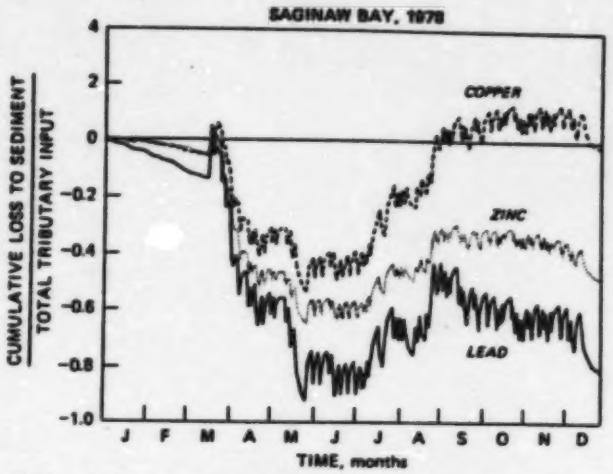

FIG. 14. Ratio of cumulative metal lost to tributary input, Saginaw Bay, 1978.

complete conservation in the water column. For example, in spite of the fact that copper had a measured partition coefficient of 50,000, the apparent net loss of copper to the sediments was approximately zero in 1978, and there was actually a net contribution to the water column in 1977 (Table 4). Even though copper partitioned to solids, and solids were lost to the sediment, this flux was offset by wind-driven resuspension of particulate copper from the sediment back to the water column, especially in 1978 (Figure 14). Thus, copper was not truly conserved in the water column in the same sense as chloride, for example; rather, this apparent conservation was caused by two opposing processes of sedimentation and resuspension.

Sensitivity Analysis

A useful method for examining the importance of the different model parameters is a sensitivity analysis. All five free parameters from the suspended solids and metals calibrations were varied by ± 50% (N was varied by ± 25% since it is an exponent). The effect of these perturbations on the sum of squared differences between model output and observed data for each mass balance variable was calculated as a percent change (Table 5). The

TABLE 5. Sensitivity analysis results, percent change in model sum of squares.

Parameter Varied	Suspended Solids	Total Metal				Dissolved Metal			
		Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead
+50%									
v_s	-1.3	-6.1	1.9	-6.6	10	.14	.17	.28	-.14
N*	200	24	-	99	100	.27	-	.82	-.54
k_R	44	8.3	3.2	16	-.46	-3.2	6.7	0	-.94
k_B	-.41	-.23	0	-.19	.13	.14	-.17	.07	0
k_p	-	-7.0	.18	-.16	.08	-18	2.8	1.0	2.2
-50%									
v_s	74	21	5.1	64	0	-.14	-.42	-.69	.14
N*	570	110	-	450	94	-1.9	-	-2.4	.41
k_R	16	-1.2	-.88	3.6	14	5.3	-13	.76	1.9
k_B	.44	-.21	0	.19	-.13	0	.17	-.03	0
k_p	-	49	-1.4	17	-.92	160	-5.5	.68	.04

* ± 25%

sum of squares was used because some of the effects were slight and would not be seen if the scores from Table 3 were used.

Suspended solids and total metals were most sensitive to variations in N, the exponent in the variable settling mechanism (Equation 4). This parameter determines the effective settling velocity for suspended solids, and hence, total metal. Changes in this parameter result in solids leaving the water column too soon (increased N) or staying in the water column too long (decreased N).

Dissolved metals were most sensitive to variations in the partition coefficient, k_p. This was especially true for copper which had the lowest partition coefficient, and therefore the highest dissolved fraction of all four metals. The effect of increasing the partition coefficient was to remove metal from the dissolved phase, thus decreasing the dissolved metals concentrations; conversely, the effect of decreasing the partition coefficient was to release metal from the particulate phase to the dissolved phase, thus increasing dissolved metals concentrations.

The depth of active sediment, D_s, was not a model calibration parameter, but an actual physical quantity that was specified externally. As D_s in the model was constant for each segment, it was also subjected to sensitivity analysis. Varying D_s by $\pm$ 50% was found to change the model sum of squares for the mass balance variables by $\pm$ 2.5%, or less.

Overall, the model was most sensitive to variations in N, and least sensitive to variations in k_B, the sediment burial rate. N exerts both direct effects on suspended solids and total metal by controlling the settling velocity and indirect effects on dissolved metal by controlling the amount of solids available for partitioning. At the opposite extreme, k_B exerts no direct control on suspended solids or metals concentrations. Indirect control of total metal and suspended solids was exerted by the sediment burial rate by removing more or less solid material from the sediment, thus affecting the amounts available for resuspension.

CONCLUSION

The feasibility of using a dynamic mass balance modeling framework to synthesize a large data base for heavy metals has been demonstrated. Given the knowledge of external sources and concentration distributions within the system, this framework helped to determine whole system fate, and the importance of mass fluxes among the inputs, water column, and sediments.

Suspended solids were found to exert significant control on metals concentrations. The degree of control was a function of the partition coefficient between adsorbed and dissolved phases of the metal, the suspended solids dynamics of the system, and the magnitude of the sediment reservoir. Decreases in water column concentrations of metals can occur due to solids adsorption and subsequent sedimentation. Increases in water column concentrations can occur due to resuspension from the sediment reservoir. These resuspension events are usually wind-driven in nature.

Depending on the degree of solids control, it is possible for the external input of a metal to appear to be conserved in the water column. This apparent behavior would not be conservation in the same sense as for a nonreactive constituent. Rather, it would be the result of opposing effects of sedimentation and resuspension processes. Furthermore, it is possible for concentrations to actually be higher than would be predicted by the conservative assumption, because resuspension acts as an unaccounted for source. Depending on the relative magnitudes of these processes, and the time scale of observation, net metals fluxes could be positive, negative, or zero between the water column and sediments.

On the basis of sensitivity analyses with the calibrated model, total metals concentrations in the water column were found to be most sensitive to settling rates of suspended solids. Dissolved metals concentrations were found to be most sensitive to the value of the partition coefficient. Metals concentrations were found to be least sensitive to the long-term burial rate of the surficial sediment layer. This is intuitively reasonable because time scales for dynamic processes in the sediments are generally much larger than for dynamic processes in the water column.

One of the management implications of this study would appear to be that a low degree of predictive success for metals concentrations as a function of external loadings should be expected for systems in which suspended solids dynamics are not well known. To relate inputs to spatial and temporal concentration distributions, it is not sufficient to know only the partition coefficient and the water circulation regime. In addition, suspended solids loading, wind regime, system morphometry, depositional zones, and sediment concentrations must be determined. It may be possible, after several comprehensive case studies on different physical systems, to develop approximate ranges

for the principal controlling parameters for given classes of water bodies. Such information could be used to estimate mass balances for systems which do not have data bases sufficiently comprehensive for detailed model applications.

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